

# DETERMINING RATE LAW

# REACTION RATE

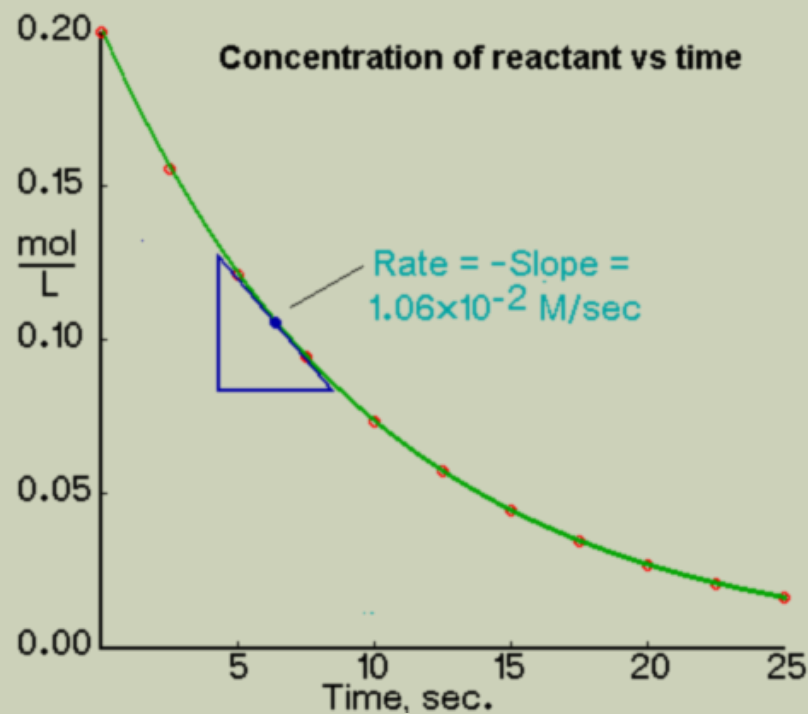
- Change in the concentration of a reactant or product per unit time

- For generic reaction  $A \rightarrow B$

$$Rate = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

- Instantaneous Rate—rate of reaction at a particular time

- Plot concentration versus time
- Slope of tangent line to curve = instantaneous rate



# RATE LAW

- Shows how the rate of a reaction depends on the concentrations of reactants
- For generic equation  $A \rightarrow B$

$$Rate = k[A]^n$$

- $k$  is the rate constant
  - Dependent on temperature
- $n$  is the rate order
- $[A]$  is the concentration of A

# RATE LAW

- Rate constant and rate order are determined experimentally
- Two types:
  - Differential rate law—expresses how the rate depends on concentration
    - Often simply called rate law
  - Integrated rate law—expresses how the concentrations depend on time

# RATE ORDERS

- Based on the effect of the concentration of reactants on the rate
- Using generic reaction  $A \rightarrow B$  as an example
- Zero order
  - Reactant concentration has no affect on the rate when changed
  - $\text{Rate} = k[A]^0$

# RATE ORDERS

## ■ First order

- Reactant concentration change is the same as the change of the rate (i.e. doubling concentration of a reactant doubles the rate)
- $\text{Rate} = k[A]$

## ■ Second order

- Reactant concentration change is half the change of the rate (i.e. doubling concentration quadruples the rate)
- $\text{Rate} = k[A]^2$

- For reactions with more than one reactant, the overall rate order is the sum of the rate orders of all the reactants

# DETERMINING RATE LAW

## ■ Method of Initial Rates

- Determines the rate order of a reactant by comparing different trials with one reactant changing and the others remaining the same
- Measures the instantaneous rate of each trial
- Often used to find the differential rate law

## ■ Graphical Method

- Graph the concentration versus time, natural log of concentration versus time, and inverse concentration versus time
- The relationship that is linear determines the rate order
- Used to find the integrated rate law

# METHOD OF INITIAL RATES

- 1) Write the generic rate law.
- 2) Find the rate order of the first reactant
  - a) Find two trials where the reactant concentration changes but the other reactant changes
  - b) Compare the rate of the two trials and the two concentrations
  - c) Solve for the exponent
- 3) Find the rate order of the remaining reactants
  - a) Find two trials where the reactant concentration changes but the other reactant changes
- 4) Write the rate orders into the generic rate law
- 5) Using one trial, solve for  $k$
- 6) Write the complete rate law



# METHOD OF INITIAL RATE EXAMPLE

Determine the rate law and the value of rate constant for the reaction at  $-10^{\circ}\text{C}$ :



Trial	$[\text{NO}]_0 \text{ (M)}$	$[\text{Cl}_2]_0 \text{ (M)}$	Initial Rate (M·s)
1	0.10	0.10	0.18
2	0.10	0.20	0.36
3	0.20	0.20	1.45

- Step 1: Write the generic rate law.

$$\text{Rate} = k[\text{NO}]^x[\text{Cl}_2]^y$$

# METHOD OF INITIAL RATE EXAMPLE

- Step 2: Find the rate order of the first reactant.
  - Choose two trials where the concentration of the reactant changed while the concentration of other reactants remain the same
    - Trials 2 and 3 → NO concentration changes and Cl<sub>2</sub> remains the same
  - Compare trials 2 and 3 in a ratio between the rates and the concentrations

$$\frac{\text{Rate (Trial 3)}}{\text{Rate (Trial 2)}} = \frac{[\text{NO}]^x (\text{Trial 3})}{[\text{NO}]^x (\text{Trial 2})} \rightarrow \frac{1.45}{0.36} = \frac{(0.20)^x}{(0.10)^x}$$

- Solve for x

$$4 = 2^x \rightarrow x = 2$$

- Rate order of NO is second order

# METHOD OF INITIAL RATE EXAMPLE

- Step 3: Find the rate order of the remaining reactant
  - Choose two trials where the concentration of the reactant changed while the concentration of other reactants remain the same
    - Trials 1 and 2 → Cl<sub>2</sub> concentration changes but NO remains the same
  - Compare trials 1 and 2 in a ratio between the rates and the concentrations

$$\frac{\text{Rate (Trial 2)}}{\text{Rate (Trial 1)}} = \frac{[\text{Cl}_2]^y (\text{Trial 2})}{[\text{Cl}_2]^y (\text{Trial 1})} \rightarrow \frac{0.36}{0.18} = \frac{(0.20)^y}{(0.10)^y}$$

- Solve for y

$$2 = 2^y \rightarrow y = 1$$

- Rate order of Cl<sub>2</sub> is first order
- Step 4: Write the rate orders into the generic rate law

$$\text{Rate} = k[\text{NO}]^2[\text{Cl}_2]$$

# METHOD OF INITIAL RATE EXAMPLE

- Step 5: Using one trial, solve for k
  - Using Trial one, plug in all the information into the rate law:

$$0.18 \text{ M} \cdot \text{s} = k(0.10 \text{ M})^2(0.10 \text{ M})$$

$$k = \frac{0.18 \text{ M} \cdot \text{s}}{(0.10 \text{ M})^3} = 180 \frac{\text{s}}{\text{M}^2}$$

- Step 6: Write the complete rate law

$$\text{Rate} = 180 \text{ s} \cdot \text{M}^{-2} [\text{NO}]^2 [\text{Cl}_2]$$

# GRAPHICAL METHOD

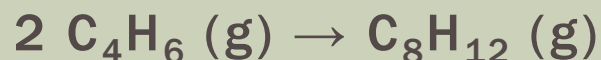
- 1) Calculate the natural log ( $\ln[A]$ ) of concentration of each reactant and the inverse concentration  $\left(\frac{1}{[A]}\right)$  of each reactant
- 2) Create three graphs: concentration versus time,  $\ln[A]$  versus time, and  $\frac{1}{[A]}$  versus time.
- 3) Graph that gives a linear relationship is the rate order

# INTEGRATED RATE LAWS

	Zero Order	First Order	Second Order
Rate Law	Rate = k	Rate = k[A]	Rate = k[A] <sup>2</sup>
Integrated Rate Law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Graph with Linear Relationship	[A] versus t	ln[A] versus t	$\frac{1}{[A]}$ versus t
Determination of Rate Constant	Slope = -k	Slope = -k	Slope = k
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

# GRAPHICAL METHOD EXAMPLE

Butadiene reacts to form its dimer according to the equation



The following data were collected for this reaction at a given temperature (seen to the right). Determine the rate order, the value of the rate constant for the reaction, and the half-life for the reaction under the conditions of this experiment.

$[\text{C}_4\text{H}_6]$ (M)	Time (s)
0.01000	0
0.00625	1000
0.00476	1800
0.00370	2800
0.00313	3600
0.00270	4400
0.00241	5200
0.00208	6200

# GRAPHICAL METHOD EXAMPLE

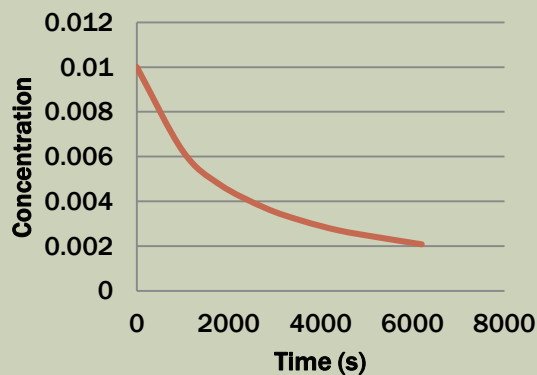
- Step 1: Calculate the natural log ( $\ln[A]$ ) of concentration of each reactant and the inverse concentration ( $\frac{1}{[A]}$ ) of each reactant

Time (s)	$\ln[C_4H_6]$	$1/[C_4H_6]$
0	-4.6	100
1000	-5.1	160
1800	-5.3	210
2800	-5.6	270
3600	-5.8	319
4400	-5.9	370
5200	-6.0	415
6200	-6.2	481

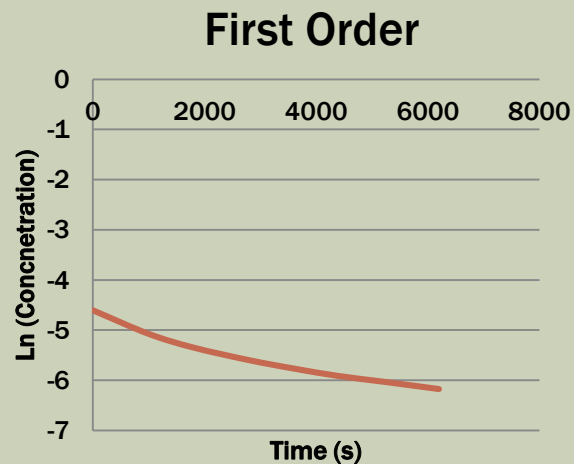


# GRAPHICAL METHOD EXAMPLE

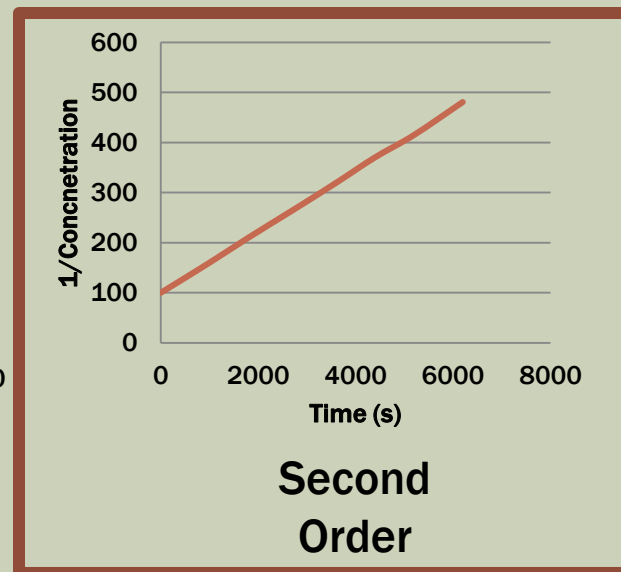
- Step 2: Create three graphs: concentration versus time,  $\ln[A]$  versus time, and  $\frac{1}{[A]}$  versus time.
- Step 3: Graph that gives a linear relationship is the rate order



Zero Order



First Order



Second Order

# GRAPHICAL METHOD EXAMPLE

- Rate law:  $\text{Rate} = k[\text{C}_2\text{H}_4]^2$
- Rate constant (k)
  - Use the slope to calculate k
  - $y = 0.0612x + 99.368$  so  $k = 0.0612 \text{ M}^{-1}\cdot\text{s}$
- Half-life

$$t_{1/2} = \frac{1}{k[\text{C}_2\text{H}_4]_0} = \frac{1}{(0.0612 \text{ M}^{-1} \cdot \text{s})(0.01000 \text{ M})}$$
$$= 1.63 \times 10^3 \text{ s}$$